Simple and Reproducible Procedure to Prepare Self-Nanostructured NiO Films for the Fabrication of P-Type Dye-Sensitized Solar Cells

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Porous and nanostructured thin films of NiO (3.5 μm thick) were prepared on FTO coated glass by annealing nickel acetate films obtained by recrystallization under hydrothermal conditions in the presence of hexamethylenetetramine. The photovoltaic performances of the NiO films were optimized with coumarin C343 as sensitizer and iodide/triodide as redox mediator and led to the following values of V_{OC}, J_{SC}, ff, and η: 117 mV, 0.88 mA/cm^2, 0.28, and 0.036% respectively, under AM 1.5. With the improved PMI-NDI dyad as sensitizer and the tris(4,4′-bis(tertbutyl)bipyridine) cobalt$^{II/III}$ couple as redox mediator, the overall photoconversion efficiency reached 0.16%. An essential advantage of this procedure lies in its good reproducibility offering a reliable strategy to test new dyes and other parameters to improve the photoconversion efficiency of this new type of DSSC.

1. Introduction

The sensitization of p-type semiconductors (p-SCs) to prepare photovoltaic cells is a new emerging and growing research area. Formally, this novel type of photoelectro-chemical cell is very attractive, because it could lead to low-cost photovoltaic devices, such as Grätzel cells, based on n-type SCs.[1] Besides, another important potential utility of p-type dye-sensitized solar cells (p-DSSC) is connected to the fabrication of tandem dye-sensitized solar cells (i.e., a n-type photoanode coupled to a p-type photocathode), whose overall photoconversion efficiencies could surpass those of convential n-DSSCs.[2,3] Indeed, a n-SC/dye$_1$/mediator/dye$_2$/p-SC tandem cell includes two different semiconductors and two different dyes; therefore, a higher photovoltage and a larger photocurrent can be delivered. Besides, sensitized p-type SC can be involved in the fabrication of photocatalytic devices for the transformation of solar energy into chemical fuels.[4] In a n-type dye-sensitized solar cell (n-DSSC), an electron is injected from the excited-state of the sensitizer to the conduction band of a n-type semiconductor (gene-rally TiO$_2$), while in a p-type DSSC, the photoexcited sensitizer is reduced by hole injection into the valence band of a p-type semiconductor. So far, nickel oxide is the most widely investigated p-type SC for the fabrication of p-DSSCs.[3,5−11] From a practical point of view, the develop-ment of this research relies on the ability to prepare good quality and reproducible nanoporous p-type semiconductor films. Toward this goal, the semiconductor film must fulfill several requirements such as a large surface area in order to chemisorb the highest amount of sensitizers, the pores of the network should be sufficiently large to provide easy access of sensitizers to the whole SC specific area, the film should be mechanically stable and strongly bound to the back trans-parent conducting electrode (e.g., FTO or ITO). Finally, the preparation of thick electrodes is another important

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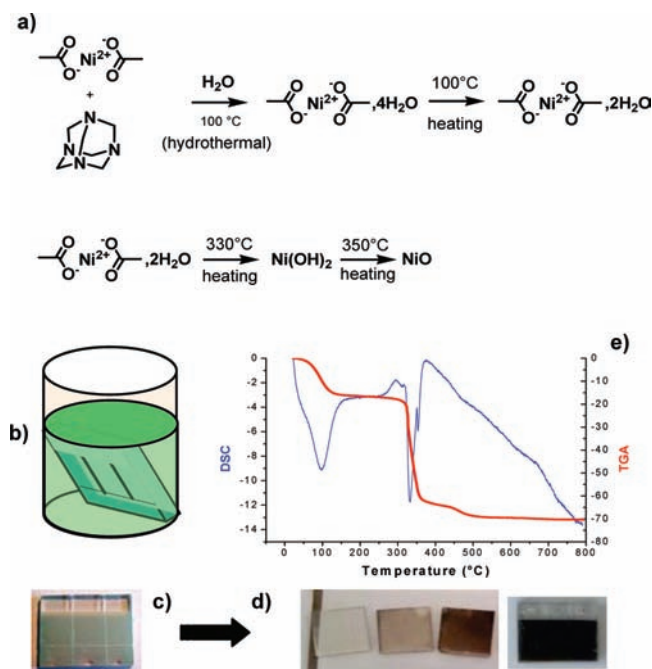
Figure 1. (a) Sketchy chemical route leading to the formation of NiO films. (b) Representation of the FTO substrate covered by a green film in the Teflon bomb after hydrothermal treatment at 100 °C. (c) 5 μm thick $Ni(OCOCH_3)_2 \cdot 4H_2O$ film after hydrothermal treatment for 300 min and before annealing. (d) NiO films prepared after hydrothermal treatment at 100 °C for 100, 150, 200, and 300 min and heating at 450 °C. The thickness increases from 0.06, to 1.0, 1.6, and 3.5 μm from left to right. (e) TGA/DSC curves of the green $Ni(OCOCH_3)_2 \cdot 4H_2O$ precursor labeled NiX in the text.

parameter to consider, because it governs the total absorbance of the electrode and therefore the amount of photo-generated charges. Usually, the preparation of nanoporous NiO electrodes for DSSCs requested several steps, that is the synthesis of the precursor (e.g., $Ni(OH)_2$) as nanoparticles, their intimate mixing in a "black box" paste in a mortar, the deposition via the doctor blade technique onto the conducting substrate, and a reactive sintering at 450 °C.[5,7,8,12–14] Nevertheless, in our hands, this technique turned out to be far from fully satisfactory. First, because it is very difficult to obtain thick and crack free NiO films, and second its reproducibility is relatively low. Several alternative routes to prepare NiO films are reported in the literature, such as chemical vapor deposition,[15] electrodeposition,[9,16] hydrothermal synthesis,[6,17,18] sputtering,[19] and sol−gel.[20] However, so far, these methods were essentially used for the

fabrication of electrochromic devices. In this work, we report an improved hydrothermal route adapted from the work of Xi and co-workers[18] to prepare in situ self-organized nanoporous NiO films on the surface of FTO coated glass substrates. We show that this technique leads to reproducible thick and crack free films which are suitable to set up p-DSSCs with good photovoltaic performances.

2. Results and Discussion

2.1. In Situ Preparation of the NiO Films on SnO:F Substrates. The synthetic route used to prepare nanostructured NiO films is summarized in Figure 1a. This protocol was inspired from the work of Xi and co-workers[18] who prepared NiO films by a two steps procedure, that is a reaction of nickel nitrate hexahydrate with hexamethylenetetramine in aqueous solution at 90 °C, followed by heating at 300 °C. In our modified protocol, $[Ni(NO_3)_2 \cdot 6H_2O]$ is replaced by $[Ni(OCOCH_3)_2 \cdot 4H_2O]$, and reaction takes place at 100 °C under hydrothermal conditions (i.e., the precursors were placed in a sealed autoclave and reacted under an autogenous pressure). This leads to the formation of a pseudo amorphous intermediate species, labeled hereafter NiX, which deposes as a green film on both sides of the FTO coated substrate (Figure 1b and 1c). The green intermediate species NiX was then converted into NiO upon heating in air at 450 °C for 30 min, which led to a colorless or dark film depending on the film thickness (Figure 1d) (vide infra). At this stage, it is worthwhile to mention that (i) the sintering temperature was set at 450 °C to enable a straightforward comparison of the physical characteristics of our photovoltaic cells with those reported in the literature,[3,6,8,21] even though this temperature is probably not optimal (vide infra) and (ii) the deposition of the green film on the FTO-electrode is strongly dependent on the sample slant in the Teflon bomb. An angle of about 45° appears optimal to give homogeneous films, while substrates layed flat remained colorless and uncovered. In our hands, this modified protocol yields thick, very adhesive, and reproducible films on FTO substrates. It is also worth mentionning that green films deposited on the surface of FTO at 90 °C by simple coprecipitation and sintered at 450 °C led to NiO films much less homogeneous, more fragile and less regular in thickness.

2.2. Characterization of the NiO Films and Their Intermediate Species. The specific surface area of NiX powder determined by the Brunauer−Emmett−Teller (BET) and the Barrett−Joiner−Halenda (BJH) methods is estimated at 22 m^2/g. Slow evaporation at room temperature of the mother liquor remaining in the reactor after hydrothermal treatment yields monocrystals, whose structure could be solved by X-ray diffraction. This study revealed the $Ni_4O_{32}C_{34}N_{12}H_{84}$ compound built upon $[Ni(H_2O)_2(OCOCH_3)_2]$ and $[Ni(H_2O)_3(OCOCH_3)_2]$ polyhedra connected via $[C_6H_{12}N_4]$ molecules. Nevertheless, based on the examination of the powder X-ray diffraction (XRD) analysis and TGA curve of the green NiX film (vide infra), this material cannot be retained as the precursor of NiO in the aforementioned hydrothermal reaction. Formally, the powder pattern of the green NiX

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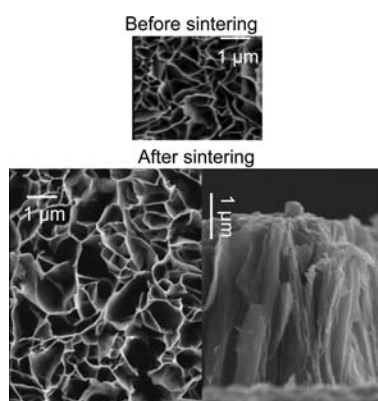
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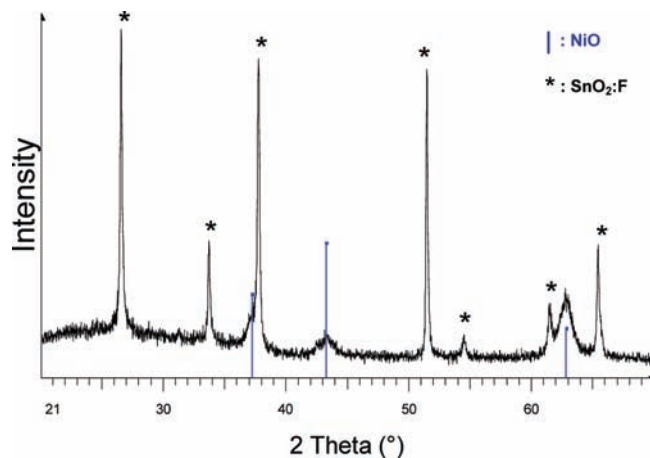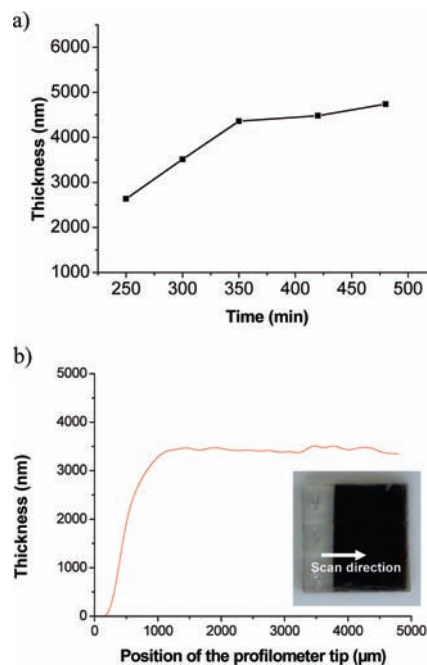
Figure 2. XRD pattern of NiO film deposited at the surface of SnO_2:F substrate.

Figure 3. (a) Top view of a $Ni(OCOCH_3)_2 \cdot 4H_2O$ film before sintering and (b) top view and side view of a NiO film after sintering at 450 °C observed by scanning electron microscopy.

Figure 4. (a) Evolution of the NiO film thickness vs the duration of the hydrothermal treatment. (b) Profilometer measurement of the NiO prepared cell after 300 min at 100 °C.

film revealed broad peaks suggesting a pseudoamorphous character associated with low crystallite sizes. Comparison of this pattern with the jcpdf database gave no hint of a known phase. On the other hand TGA measurements (Figure 1e) suggest a $Ni(OCOCH_3)_2 \cdot 4H_2O$ formula for NiX, that is, nickel acetate tetrahydrate, the starting materials. Thermal analyses evidence weight losses of 16.6%, 63.4%, and 70% at about 100, 330, and 350 °C, respectively. This can be explained on the basis of the successive departures of two water molecules and ~0.3 free physisorbed water molecules, two acetic acid molecules, and one water molecule giving rise to NiO as final product with $Ni(OCOCH_3)_2 \cdot 2H_2O$ and $Ni(OH)_2$ as intermediate species. Thus, the hydrothermal treatment would trigger the stabilization of a new crystalline form of nickel acetate tetrahydrate which structure cannot be determined due to the bad crystallized state of our sample. At this stage, let us mention that pure NiO may be also prepared at 350 °C (as predicted from DSC curve) by prolonged thermal treatment at this temperature. The sintering temperature of 450 °C, commonly used in the literature, appears here as overestimated and could be lowered, which should favor higher specific area for NiO (vide supra). Moreover, it is worth noticing that the presence of hexamethylenetetramine is required to condense in situ the new allotropic form

of nickel acetate tetrahydrate at the surface of the FTO substrate.

The XRD pattern of the NiO film deposited on the FTO substrate after a 300 min hydrothermal treatment and sintering at 450 °C is depicted in Figure 2. Diffraction peaks can be assigned without any ambiguity to the NiO material[22] and SnO_2:F substrate. No byproduct is detected. A refinement of the XRD pattern based on the fundamental method[23] led to average crystallite size of 11 nm. NiO films (and $Ni(OCOCH_3)_2.4H_2O$ films) were also examined by SEM. Representative pictures are given in Figure 3. As previously reported by Xi et al.,[17] the spongy, cavernous features of gypsum flower is highlighted, with ~10 nm thick nanoleaves. Overall, these NiO sheet-like films are very similar to those observed for the green precursors. Naturally, this suggests that the nanolayered structuration stems in direct line from the complexation process at the very first steps of the hydrothermal synthesis. Let us notice here that a very feature of this preparation method of NiO concerns the tunability of the film thickness with the hydrothermal reaction time as depicted in Figure 4a. The dependence of the thickness on the reaction time is linear until 350 min affording a homogeneous film of 4.4 μm thickness. Beyond 350 min, a plateau is reached and the film thickness does not increase anymore. Rewardingly, a 3.5 μm thick film, crack-free, strongly adherent to the electrode (i.e., stable under a harsch finger friction) is already satisfactory as it is thicker than most of the previously reported values for nanoporous NiO films. It is worthwhile to note that the reproducibility of the film thickness is very good with this method. For example,

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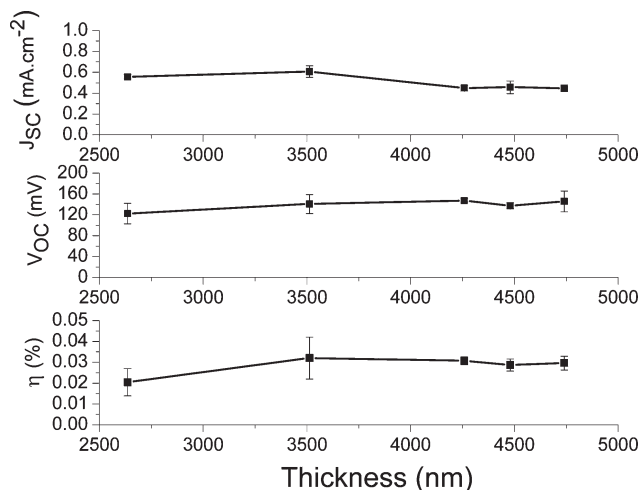
Figure 5. Variations of J_{SC}, V_{OC}, and η as a function of the thickness of the NiO photocathode. The solar cells performances were recorded under simulated solar irradiation AM 1.5 (100 mW/cm^2). Sensitizer: coumarin C343. Electrolyte: [LiI] = 0.5 M and [I$_2$] = 0.1 M in propylene carbonate.
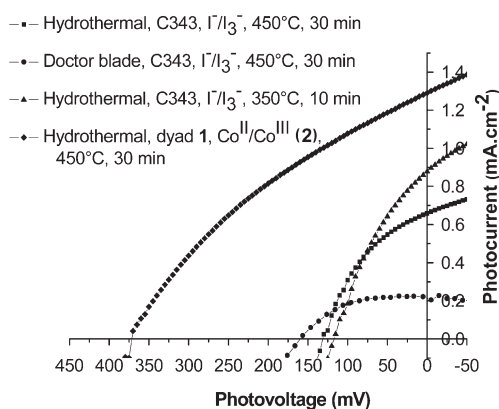
Figure 6. Photocurrent−photovoltage characteristics of solar cells recorded under simulated solar irradiation AM 1.5 (100 mW/cm^2). Sensitizer: coumarin C343 or dyad **1**. Electrolyte: [LiI] = 0.5 M and [I$_2$] = 0.1 M or [**2**] = 0.1 M, 10% oxidized with NOBF$_4$ in propylene carbonate. (Electrode thickness: Hydrothermal = 3.5 μm, Doctor blade = 0.6 μm).

within 14 different films prepared for a reaction time of 300 min, the average thickness was 3.5 μm, the thinner film was at 3.42 μm and the thicker was at 3.53 μm (deviation was therefore lower than 100 nm). The thickness profile of a FTO substrate partly covered by a 3.5 μm NiO film is depicted in Figure 4b. The low surface roughness of the deposited coat, as well as the steep step at the electrode/NiO interface is well evidenced and is reproducible, whatever the probed area.

The specific surface area of the 3.5 μm thick NiO film, determined by the Brunauer−Emmett−Teller (BET) and the Barrett−Joiner−Halenda (BJH) methods is estimated at 61 m^2/g, a value which compares well with some TiO$_2$ films used for n-DSSC.[24] This value is three times larger than for NiX. Moreover, the measured porosity reveals a narrow Gaussian pore size distribution centered at 8 nm with a full width at half-maximum of about 6 nm.

2.2. Application of the NiO Films to DSSCs. To assess the suitability of the above NiO electrodes to fabricate

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Table 1. Photovoltaic Performances of DSSC Devices Based on NiO Electrodes[a]

NiO preparation	dye/redox mediator[b]	V_{OC} (mV)	J_{SC} (mA/cm^2)	ff (%)	η (%)
A	C343/iodide	160	0.20	31	0.010
B	no dye/iodide	< 5	0.04	n. m.	< 610^{-5}
B	C343/iodide	140	0.66	38	0.032
C	C343/iodide	117	0.88	35	0.036
B	**1/2**	370	1.3	34	0.16

[a] A: NiO prepared by the doctor blade method and sintered at 450°C. B: NiO prepared by the hydrothermal method and sintered at 450°C. C: NiO prepared by hydrothermal method and sintered at 350°C. n.m. = not measurable. [b] Iodide refers to the mixture I$_3^-$/I$^-$.

dye-sensitized solar cells, we used the coumarin C343, since it proved to be one of the best performing sensitizer among the commercially available dyes and also for straigtforward comparisons with other reported p-type DSSCs.[7,8,13,21] To optimize the film preparation, the open circuit photovoltage (V_{OC}), the short circuit photocurrent (J_{SC}), and the overall photoconversion efficiency (η) were measured as a function of the thickness of the NiO film (Figure 5). The V_{OC} slightly increases as the film becomes thicker, while the J_{SC} is maximum for 3.5 μm. Since the optimal overall photoconversion efficiency was measured for a 3.5 μm thickness, we conclude that the optimal reaction time to prepare NiO photocathodes corresponds to 300 min.

Figure 6 shows the photocurrent−photovoltage characteristics of solar cells prepared by the hydrothermal method and with the conventional "doctor blade" technique.[10−12] The photovoltaic performances of the cells are gathered in Table 1.

Our results with the doctor blade technique are similar to the best performances published for p-DSSC with C343.[7,8,13] However, the hydrothermal method described herein affords a significantly higher overall photoconversion efficiency than the doctor blade technique (Table 1 and Figure 6).

The higher overall η obtained with the hydrothermal method essentially stems from a larger J_{SC}. The large surface area and the densely interconnected network of NiO lamella certainly provide a high loading of the dyes along with an efficient transport of the injected holes to the back conductive FTO electrode. But, most importantly, the preparation of the NiO electrodes by this hydrothermal method is reproducible, a feature which is not shared by the doctor blade technique.

The reproducibility of this NiO preparation was evaluated by the measurements of V_{OC}, J_{SC}, ff, and η within a series of 9 different NiO photoelectrodes prepared from 9 different batches. As pictured in Figure 7, the deviation is relatively narrow for all the characteristics of the solar cells, with a V_{OC} and ff however more stable than J_{SC}. Other attractive features of this method of NiO preparation concern (i) the thickness of the nanoporous film that can be adjusted by simply controlling the reaction time and (ii) the much thicker, crack-free and mechanically stable films (up to 3.5 μm) that can be obtained. Interestingly, as also observed by others,[12,21] we note that thicker NiO films are particularly dark (Figure 1d), but contrary to our initial thoughts, this is not a drawback for their utilization in p-DSSC since these electrodes give good photovoltaic performances. Naturally, the dark electrodes
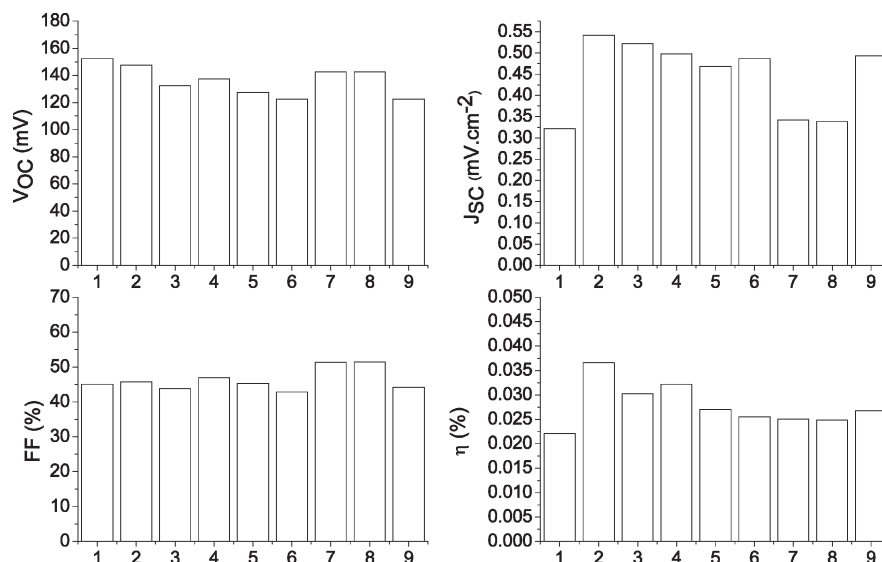
Figure 7. Evolution of the characteristics of nine different solar cells prepared in the same conditions but issued from nine distinct batches (i.e., hydrothermal treatment at 100 °C for 300 min followed by a sintering at 450 °C for 30 min) with C343 as dye and iodide/triiodide as redox mediator.
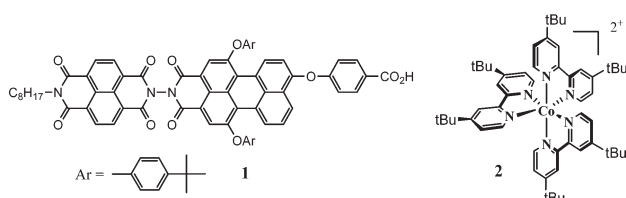
Figure 8. Structures of the dyad **1** and of the cobalt redox mediator **2**.

without sensitizer give no detectible photocurrent (entry 2, Table 1), underlying as expected, the determinent role of the dye. Usually, in electrochromic devices based on nickel oxide, the color changes correspond to the oxidation of Ni(II) (transparent) to Ni(III) (brownish).[12,25] In the present study, no Ni(III) traces were detected by XPS. Consequently, the black color of the thick film cannot be explained on the basis of the existence of such cations. This agrees with results reported by Korosec and co-workers,[25] who speculated that materials treated at temperatures higher than 230 °C gave very poor electrochromic effects (i.e., a low ability to stabilize Ni(III) cations).

Let us notice also that a slight decrease in the sintering temperature significantly enhances the photovoltaic performances. Hence, sintering at 350 °C for 10 min instead of 450 °C for 30 min, led to cells with V_{OC}, J_{SC}, and η values of 117 mV, 0.88 mA/cm^2, and 0.036%, respectively. As the sintering temperature is lowered, we assume that more dyes are grafted on the final NiO film which could account for the higher performances. Indeed, the BET analyses showed a larger surface area at lower sintering temperature (i.e., 160 and 120 m^2/g for the green precursor powders deposed in the bottom of the reactor and sintering temperature 350 or 450 °C respectively).

Finally, these new NiO electrodes prepared by the hydrothermal method were tested with improved sensitizer and electrolyte, recently published.[26] The dyad **1** is

composed of a perylene monoimide sensitizer connected to a naphthalene diimide electron acceptor. On NiO, this dyad yields to a particularly long-lived charge separated state (microsecond range), which is particularly important to efficiently donate its electron to the redox mediator in solution.[10,26] On the other hand, the potential of the redox couple Co^{III}/Co^{II} of the cobalt complex **2** is more negative than that of I$_3^-$/I$^-$ and consequently enables to increase significantly the photovoltage of the cell (Table 1). Using dyad **1** as sensitizer and cobalt complex **2** as redox mediator (Figure 8), the photovoltaic performances of the cell are greatly enhanced relative to those obtained with C343 with I$_3^-$/I$^-$, since the photovoltage reached 370 mV while producing a photocurrent value of 1.3 mA/cm^2, leading to an overall photoconversion efficiency of 0.16%, which lies among the best performances obtained with a p-DSSC. This result shows that this method of NiO preparation is also suitable with improved materials and can be notably used to test new dyes and electrolytes.

Conclusions

We have successfully demonstrated the implementation of a modified hydrothermal synthesis to obtain self-organized nanoporous NiO films which proved to be suitable for the reproducible fabrication of DSSCs. The thickness of the electrode is well-controlled and can reach values as large as 3.5 μm with no crack. The photovoltaic performances of the solar cells made with these NiO films are higher than those obtained with the traditional doctor blade technique. We believe that this new method of fabrication of nanoporous NiO electrodes will be useful to investigate new sensitizers and new electrolytes to design and construct more efficient p-DSSCs.

Experimental Section

Materials. Nickel acetate tetrahydrate, hexamethylenetetramine, coumarin C343, lithium iodide, iodine, propylene carbonate, and methoxyacetonitrile were purchased from Aldrich or Acros and were used as received. Conductive glass substrates

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(F-doped SnO_2) were purchased from Solems, 5 Ω/square. Dyad **1**[10] and complex **2**[10,26] were prepared as described previously.

Preparation of the NiO Films on SnO:F Substrate. Conductive glass substrates were successively cleaned by sonication in acetone, distilled water, and ethanol for 10 min before drying under vacuum. The 2.5×2.5 cm^2 substrates were then placed in a 3.2 cm wide and 4.7 cm high cylindric Teflon bomb filled at 70% with a 0.25 M nickel acetate/hexamethylenetetramine aqueous solution (Figure 1a). The bomb was then sealed in an autoclave, and heated at 100 °C for 300 min in an oven, before quenching in air at room temperature. This protocol led to the deposition of a green film of nickel acetate tetrahydrate at the surface of the FTO substrate (both sides). This film was then heated in air at 450 °C (or 350 °C) for 30 min, leading to colorless or dark films depending on the film thickness (Figure 1d). When the cobalt complex was used as redox mediator, a dense underlayer of NiO was deposited on the FTO electrode prior to the formation of the porous NiO film. This was achieved by spin-coating a saturated ethanol nickel acetate solution followed by sintering at 450 °C for 30 min.

Characterization. X-ray diffraction (XRD) measurements were performed on a D8 Brüker diffractometer employing the $CuK-L_3$ radiation (germanium monochromator) and a Vantec multigap detector in the 5−80° 2θ range.

BET/BJH analyses were done in a micrometrics ASAP 2010.

Powder densities were evaluated with a Micromeritics Accupyc 1330 equipment.

ATG/DSC measurements were carried out under air flow with a Setaram TGDSC 111 at a heating rate of 10 °C/minute in the 20 °C-800 °C temperature range.

SEM images were taken with a JEOL JSM-6400F microscope.

Thickness measurements were determined thanks to a Digital instrument Dektak 8 profilometer. Data analysis was done with the Dektak software, version 8.34.

Photovoltaic Cell Preparation and Characterization. The doctor blade NiO electrodes were prepared by a method published previously.[10−12] After sintering and cooling to room temperature, the NiO electrodes were immersed in a 0.01 M C343 solution in acetonitrile at room temperature for 16 h. Then, the dyed electrodes were thoroughly rinsed with acetonitrile. The counter electrode was a platinum film sputtered on a FTO glass electrode. The active surface area of the cell was 0.8 cm^2. Cells were made by clamping the photoanode with the platinum electrode with the interlayer space filled with an electrolyte. The electrolyte composition is a mixture of 0.5 M LiI, 0.1 M I_2 or of 0.1 M **2**, 0.01 M $NOBF_4$ and 0.1 M $LiClO_4$ in propylene carbonate. The current−voltage characteristics of the cells were measured by a Keythley model 2601 digital sourcemeter controlled by Labview: 2.0 software. The photovoltaic cell was illuminated with an Oriel lamp calibrated to AM 1.5 (air mass) intensity (1000 W.m^{-2}). Cells were biased from −500 to +100 mV, with 5 mV steps and a 100 ms settling time.